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Biomimetic Synthesis of Water Soluble Conductive Polypyrrole and Poly(3,4-Ethylenedioxythiophene)

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ABSTRACT

A novel biomimetic method for the synthesis of conducting molecular complexes of polypyrrole (PPYR) and poly(3,4-ethylenedioxythiophene) (PEDOT) in the presence of a polyelectrolyte, such as polystyrene sulfonate (SPS) is presented. A poly(ethylene glycol) modified hematin (PEG-Hematin) was used to catalyze the polymerization of pyrrole (PYR) and 3,4-ethylenedioxythiophene (EDOT) in the presence of SPS to form PPYR/SPS and PEDOT/SPS complexes. UV-VIS, FT-IR, and electrical conductivity studies for all complexes indicated the presence of a stable and electrically conductive form of these polymers. Furthermore, the presence of SPS in this complex provides a unique combination of properties such as processability and water-solubility.

Key Words: PEDOT; Pyrrole; Polypyrrole; Synthetic enzyme; Hematin; Conductive polymers.

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INTRODUCTION

The increasing environmental concern of hazardous chemical wastes, has led to an upsurge in efforts towards the development of biochemical "green chemistry" alternatives for the synthesis of electronic and photonic polymers. Enzymatic polymerizations have attracted much attention with oxidative enzymes, such as horseradish peroxidase (HRP), being used for the synthesis of polyanilines and polyphenols through oxidative free radical coupling reactions.[1–3] The proposed mechanism for HRP catalyzed polymerization involves the interaction of the heme-iron cofactor of the enzyme with the peroxide yielding an oxidized heme-iron complex.[4] Subsequently, the oxidized heme-iron complex reacts with the substrate in a one-electron transfer reaction to produce the substrate radical and a new iron-heme complex. The coupling of the substrate radicals leads to the formation of the polymer. However, to date this enzymatic approach could not be extended to polythiophenes or polypyrroles (PPYRs),[5] which have been reported to have high electrical conductivity and are of significant technological importance.[6] This was due to the fact that monomers such as 3,4-ethylenedioxythiophene (EDOT) and pyrrole (PYR), complexed with the active site of the enzyme catalyst, causing deactivation of the latter and thus proving to be unsuitable substrates for this enzymatic approach. This deactivation phenomenon thus drastically limits the prospects for the enzymatic synthesis of other conductive polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT), which is of interest for transparent, antistatic conductive coatings and polymers based on PYR for organic batteries and display devices.[6]

Encouraged by the numerous reports based on the common scenario of Fe^{2+} catalysts, we have investigated the prospect of biomimetic catalysts, which would effectively simulate the action of enzymes but offer greater stability, lower cost, and more versatility in a similar eco-friendly manner. We thus have explored the use of hematin, which serves as a catalytic center of redox enzymes such as catalase, cytochrome C, etc. There have been reports of the use of different forms of hematin for catalysis, in aqueous conditions, but the catalytic activity was observed to be much lower than that of the enzyme.[7–9] Additionally, Akkara et al. has reported the efficient synthesis of polyaromatic compounds catalyzed by hematin in mixed solvent systems or buffer systems of high pH values.[10] We had previously reported the use of a chemically modified hematin called poly(ethylene glycol)-hematin (PEG-Hematin) functioning as a "syn-enzyme" to effectively synthesize conducting polyaniline in the presence of polyelectrolye templates.[11] We report here further modification of this artificial catalyst towards the synthesis of conducting PEDOT and PPYR with the ultimate goal of expanding the versatility of this catalyst.

Moreover, a unique template assisted approach for the synthesis of water-soluble polymers has been reported from our laboratories involving the enzymatic polymerization of aniline and phenol with HRP as the catalyst in the presence of an anionic polyelectrolyte.[12] In this case, the polyelectrolyte, such as polystyrene sulfonate (SPS), serves several functions, namely it enables the electrostatic alignment of the aniline monomers to promote a *para* directed coupling, provides counterions for maintaining charge neutrality in the doping process and complexes with the polymer to maintain water solubility. Aside from the polyelectrolyte macromolecular templates, initially studied, micellar templates such as sodium dodecylbenzene sulphonic acid and biological templates like DNA were also investigated. These templates have been reported to be successful as providing nanoreactor types of sites in the one-pot enzymatic synthesis of conducting polyanilines,[13] where, the template provided a "local" environment wherein the pH and the charge density near the template molecule was different and preferable to that of the bulk solution.

In this paper, we report, a novel synthesis of water soluble PEDOT and PPYR using PEG-Hematin as an efficient catalyst in the presence of SPS as a template. UV-VIS and FT-IR spectroscopy and electrical conductivity studies were used to characterize the polymer. Additionally, we have copolymerized EDOT and PYR using this unique catalyst and electrical conductivity of this copolymer is reported.

EXPERIMENTAL

Hematin was purchased from Sigma Chemical Co. (St. Louis, MO). Pyrrole (PYR, purity 99.5%), EDOT monomer (purity 99.5%), SPS, PEG and hydrogen peroxide (30%) were purchased from Aldrich Chemicals Inc., Milwaukee, WI and were used as received. All other chemicals were purchased from Aldrich and were of reagent grade or better. Poly(ethylene glycol)-hematin was synthesized according to the procedure previously published.[14]

The polymerization of PYR or EDOT, in the presence of SPS was catalyzed by PEG-Hematin at 25°C using hydrogen peroxide under ambient conditions. Polystyrene sulfonate (36.8 mg) was dissolved in deionized water (10 mL) at pH 1.0 for the polymerization of EDOT (concentration 0.2 mM) and at pH 2.0 for the polymerization of PYR (0.2 mM). This was followed by the addition of 5 mg of PEG-Hematin to this solution. The polymerization was initiated by the addition of several aliquots of 800 μL of 0.03% hydrogen peroxide added in several small increments. The reactants were stirred for 8 hours to complete the polymerization followed by dialysis using Centricon concentrators (10,000 cut off, Amicon, Inc., Beverly, MA). The samples were then dried under vacuum at 60°C and used for further analysis. The gravimetric yield was typically 95% or higher. A similar procedure was used for the copolymerization, in the presence of SPS, of EDOT/PYR (ratio 1 : 1).

All UV-VIS spectra were obtained using a Perkin-Elmer Lambda 9 UV-VIS-near IR spectrophotometer. The FT-IR measurements were carried out on films cast on a ZnSe disk using a Perkin-Elmer FT-IR spectrophotometer. Conductivity measurements were performed on pellets using a standard linear four-point probe with a Keithley 619 electrometer/multimeter.

RESULTS AND DISCUSSION

The polymerization reaction of EDOT was monitored spectroscopically in an aqueous solution at pH 1.0 and the spectral changes are shown in Fig. 1. As seen in the figure the monomer did not show significant absorption. However, initiation of polymerization by the addition of H_2O_2 led to the appearance of absorption from 600 to 1200 nm. This was also accompanied by the change in the color of the reaction solution to a dark blue color with a simultaneous increase in the absorption intensity of the peaks over time. The broad band at 700 nm with a large absorption tail around 1200 nm was attributed to the π–π^* transition in the polymer chain.

The FT-IR spectrum (Fig. 2) collected after polymerization showed absorption at 1342, 1218, and 976 cm^{-1} all assigned to doping interaction of SPS.[15] The most

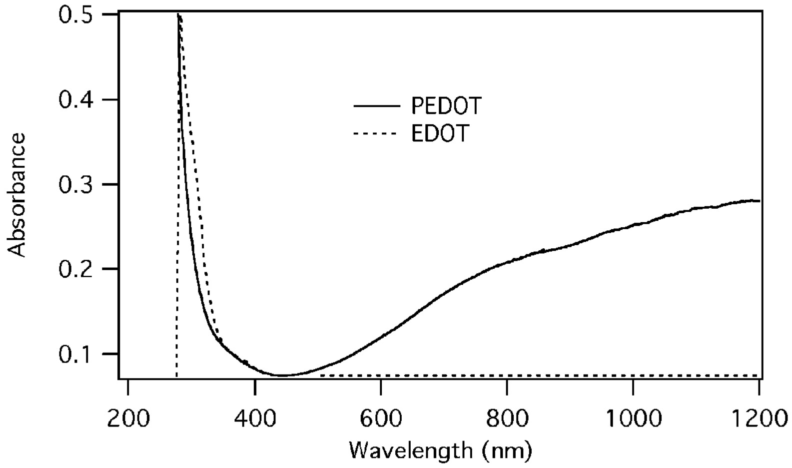

Figure 1. UV-VIS of monomer EDOT and polymer PEDOT.

significant feature, however, was the absence of bands at the range of 1600–1800 cm^{-1} indicating that no over-oxidation or ring opening had occurred.

The UV-VIS spectrum of the water-soluble SPS/PPYR is shown in Fig. 3. A broad band at 900 nm was assigned to an extended conjugation in the backbone of the PPYR. Moreover, conjugation was also confirmed by the FT-IR spectrum of the polymer (Fig. 4), wherein the peaks at 1480/1540 cm^{-1}, are assigned to the symmetric and anti-symmetric ring stretching mode, respectively.[15]

The electrical conductivity data for the PEDOT (1×10^{-5} S/cm) and PPYR (1×10^{-4} S/cm) polymerized with PEG-Hematin were determined using a four-point probe. In addition studies involving copolymerization of EDOT with PYR were initiated. The UV-VIS spectrum (Fig. 5) of this copolymer showed a large absorbance in the range

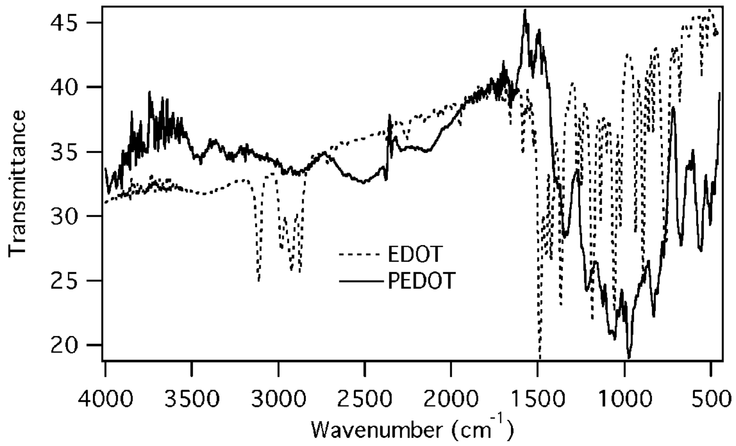

Figure 2. FT-IR of monomer EDOT and of polymer PEDOT in presence the of SPS.

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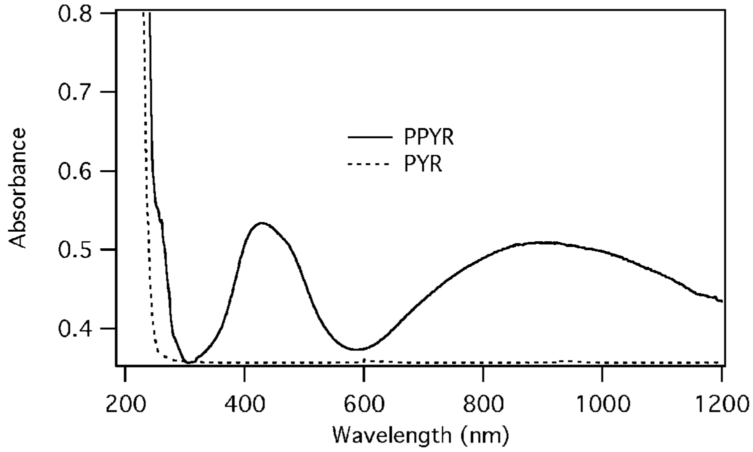

Figure 3. UV-VIS of monomer PYR and polymer PPYR.

400–900 nm while the conductivity measurements of this copolymer were substantially improved and found to be in the range of 0.1–1.0 S/cm.

Further investigations are being carried out on these copolymers and are focused on the enhancement of the conductivity and improvement of other physical properties of these copolymers systems.

CONCLUSION

In summary, a novel biomimetic method for the synthesis of conducting molecular complexes of PPYR and of PEDOT in the presence of a polyelectrolyte, such as SPS is

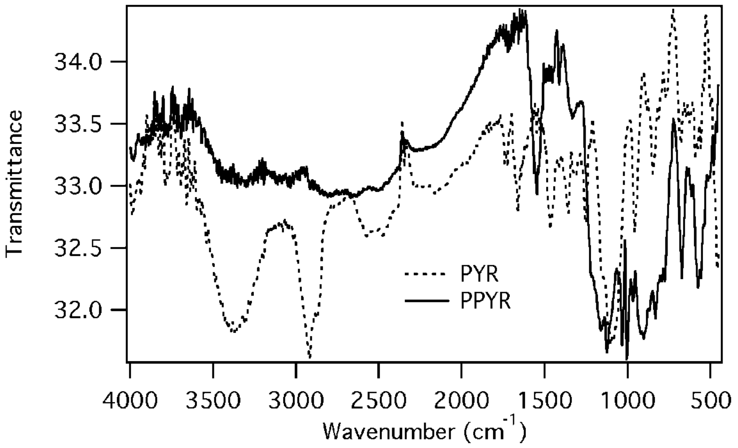

Figure 4. FT-IR of monomer PYR and of polymer PPYR in the presence of SPS.

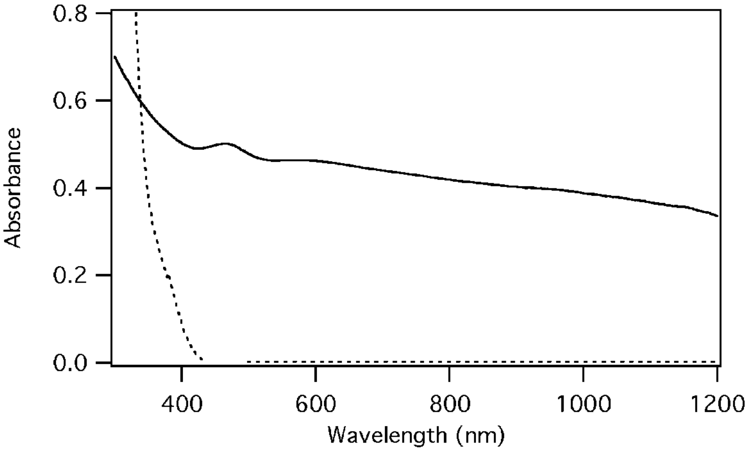

Figure 5. UV-VIS of monomer EDOT and copolymer PEDOT/PPYR/SPS. Pyrrole has similar UV of EDOT.

presented. A PEG-Hematin was used to catalyze the polymerization of PYR and EDOT in the presence of SPS to form PPYR/SPS and PEDOT/SPS complexes. UV-VIS, FT-IR, and electrical conductivity studies for all complexes indicate the formation of the electrically conductive form of these polymers. Copolymers of EDOT and PYR have also been synthesized and these novel materials have been shown to exhibit high electrical conductivity, with a unique combination of properties such as processability and water-solubility.

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